# PREPARATION AND TIO$_2$ COATING OF NANOSIZED MAGNETIC PARTICLES

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## Abstract

Nano-sized iron oxide particles such as maghemite $\gamma$-$Fe_2O_3$, hematite $\alpha$-$Fe_2O_3$ and magnetite $Fe_3O_4$ are well known for their multiple applications such as; medicine, catalysis, sensors, memory devices and electronics. In photocatalytic properties, these particles play important role as holder for photocatalytic compounds, such as co-dopped $TiO_2$. In order to maintain high surface area of such photocatalytic compounds and to get easy and economic process of restoring photocatalysts from the cleaning system utilizing their magnetic behaviour, these particles are used for also preparing core-shell catalysts. In present study, the nanosized iron oxide particles are synthetized by precipitation of Mohric salt $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ with sodium hydroxide solution and later in the process they are coated with nanosized $TiO_2$. XRD, SEM and pH measurements are used in this study.

**Keywords:** Nanosized Iron oxide particles, $TiO_2$, core-shell catalyst, Mohric salt

## 1. INTRODUCTION

Formation of nano-sized iron oxides particles (ionp) such as maghemite $\gamma$-$Fe_2O_3$, hematite $\alpha$-$Fe_2O_3$ and magnetite $Fe_3O_4$ is of great interest for their multiply use for industrial applications. These applications include their use in vitro in medicine [1], multiple catalysis tasks [2], sensors development [3], and memory devices and electronics parts [3,4]. Among many advantageous properties of these nanoparticles such as high surface volume, ease of surface modification and adsorption properties, the magnetization behavior plays significant role for their application.

The importance of the ionp is reflected in several studies for synthetic methods. The preparation and tailoring of the ionp were developed with methods including coprecipitation, microemulsion, laser pyrolysis and hydrothermal synthesis [5, 6]. The most common technique is coprecipitation where ferrous and ferric salts in water solutions have been reported to produce quite uniformed particles with ranging size between 10nm to 150 -200 nm [7, 8, 9]. The coprecipitation is kinetically driven process, influenced by chemical reaction rate, therefore to monitor chemical reaction and control of produced iron oxides and size distribution together with their magnetic properties is of great interest. Moreover, in recent times the $TiO_2$ coating of such particles plays a role in production of easily magnetically separable powdered photocatalysts. This work depicts the production of nanosized magnetic particles using the precipitation of solution of mohric salt and sodium hydroxide. Prepared particles are covered with Isopropyltitanium alkoxide and sintered in furnace for 3 hours in temperature of 360°C. SEM, XRD and pH titration curves are discussed in this study.

## 2. SYNTHESIS PROCEDURE

For synthetizing and covering of magnetic particles following chemicals were used in this study. Purchased from Sigma Aldrich: $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ pure, NaOH p.a., Titanium Isopropoxide (TIPP) 99,5% purity, $H_2SO_4$ 96 % purity, isopropanol 99,7% purity and demineralized water.

### 2.1. Preparation of magnetic nanoparticles

For preparing the magnetic particles, earlier described method was used [10]. Stock solution of Mohric salt was prepared with concentration of 0.03 mol·dm$^{-3}$. The yellow to orange colored solution was stabilized adding droplets of sulfuric acid to reach pH ≤ 3 resulting in transparent colorless solution. Stock solutions of NaOH was prepared with concentration of 0.1 mol·dm$^{-3}$. For reaction apparatus consisting of three necked flask with thermomether, heater and bubble cooler was used.

For preparation of magnetic particles,150 ml of stock solution of Mohric salt were added to three necked flask, the flask was closed and heater and cooler were turned on. When heated solution started to boil, stock solution of NaOH was added stepwisely, measuring the volume of basis solution added in each step. After each step, sample of solution from apparatus was taken and cooled down to 25°C in water bath in order to measure pH. When first magnetic particles appeared, these were collected for the XRD analysis and the reaction was stopped after reaching pH ≥ 10.

### 2.2. Covering of magnetic particles using $TiO_2$

Prepared magnetic particles were magnetically separated from the solution and directly covered by TIPP using the mass ratio of particles and TIPP 1:3. Calculated amount of TIPP was mixed with 10 ml of isopropanol and prepared magnetic particles were added to the solution. After that, the solution was ultrasonified in sonication bath for 20 minutes and then heated to 45 – 50°C for 1 hour.

After evaporation of solvent from solution the beaker with solution was placed into the crucible and temperature was elevated to 360°C with heat ramp of 10°C per minute and temperature threshold was set to 180 minutes after reaching 360°C. Cooled particles were analyzed by XRD and SEM to verify if, the coating was successful.

## 3. RESULTS

### 3.1. Measurement of pH

Figure 1 depicts the measurement of pH upon addition of sodium hydroxide.

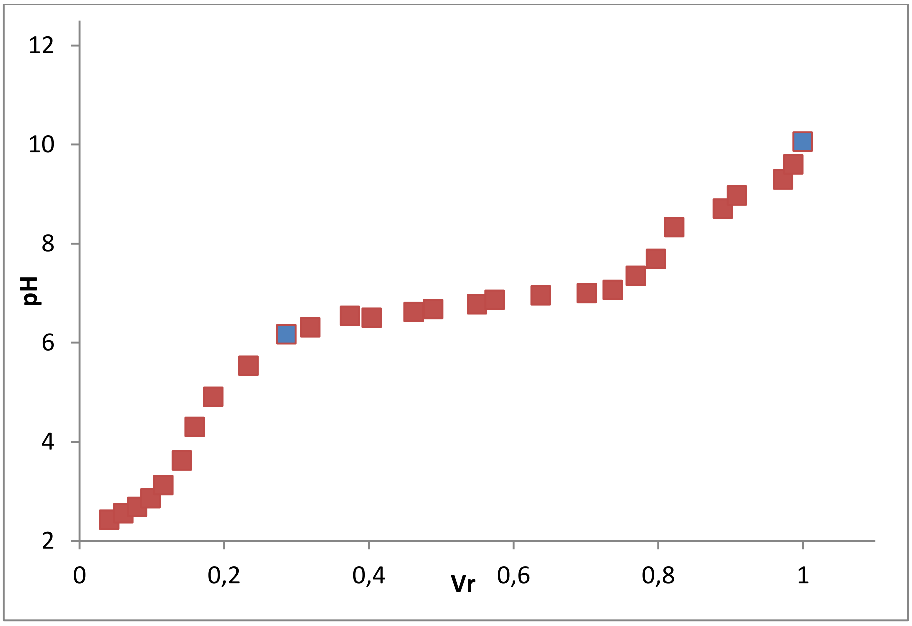

**Fig. 1** Measurement of pH

Relative volume of hydroxide added $V_r$ is used in the fig. 1 for constructing the titration curve. Two points are marked, where the magnetic particles were collected for the XRD analysis. Equation below depicts the relative volume evaluation.

$$V_r = \frac{V_a}{V_t}$$

$V_a$ stands for volume of hydroxide added, $V_t$ stands for total volume of added hydroxide in measurement.

### 3.2. XRD analysis

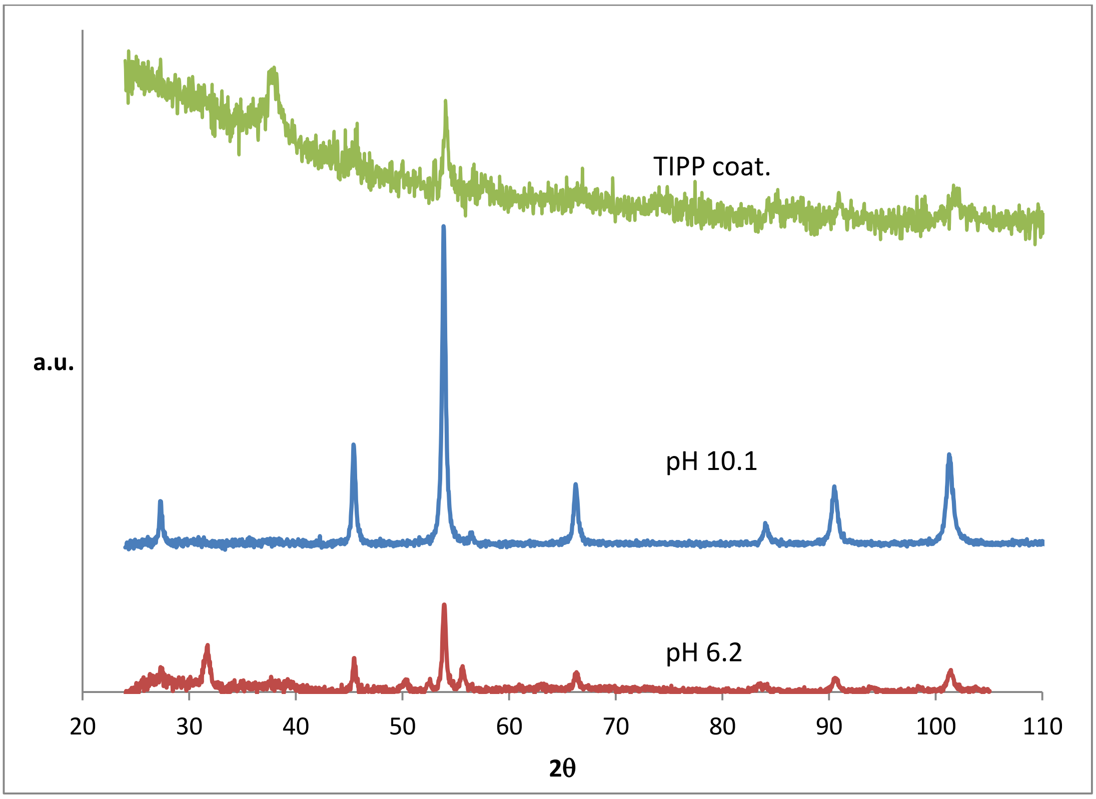

**Fig. 2** Measurement of pH

Figure 2 shows the XRD spectra of two samples and TIPP coated. pH of solution when first magnetic particles were formed was 6.2 and second sample was taken when pH was 10.1. XRD of coated particles is marked as TIPP coat. Coating of particles formed at pH 10.1 was performed only due to the fact, that XRD revealed only magnetite pure phase presented in sample. Drop in quality of XRD measurement is believed to be caused by probability, that part of the $TiO_2$ presented on the surface of magnetic particles can be presented in amorphous phase.

### 3.3. SEM analysis

On Fig. 3 the comparison of developed nanoparticles of Magnetite and magnetite coated by TIPP can be observed. Prepared magnetite particles are round shape with mean particles diameter around 0.1 μm.

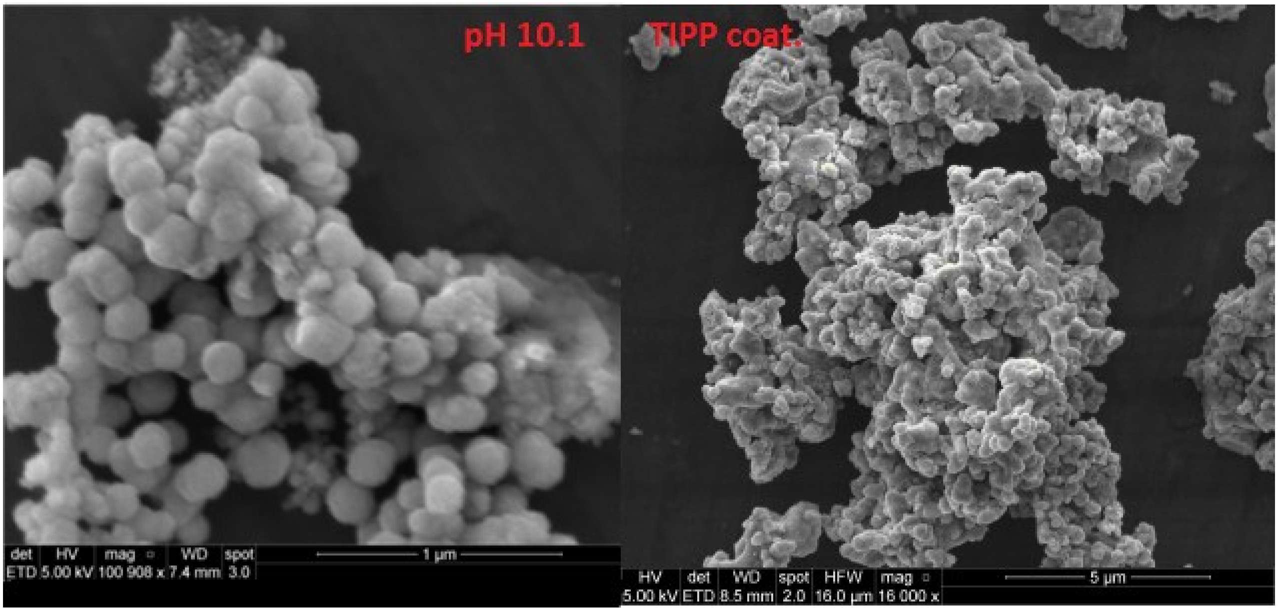

**Fig. 3** SEM analysis of prepared samples

After coating of particles the size distribution changes creating the flake shaped particles with higher size distribution than prepared magnetite nanoparticles. Different magnification is used in the figure.

## 4. DISCUSSION

In figure 1 the region of formation of magnetic particles can be observed in pH region of 5.0 – 9.5. This corresponds to the formation of first magnetic particles in sample with pH 6.2. With increasing amount of hydroxide added, the color of solution turned from dark orange through dark green to black. At the end of the synthesis, the solution was clear with sedimenting black particles, highly attracted by magnetic forces. Concerning the anaerobic conditions in boiling solution with cooler, the $Fe(OH)_2$ is formed by reaction of hydroxide with Mohric salt solution at pH region 6.0-8.0. Consumption of $OH^-$ groups can be attributed to the formation of inverse spinel orientated magnetite $Fe_3O_4$ from the pre-hydroxylated $Fe(OH)_2$, which was responsible for the dark green color of solution during the synthesis in pH region of 6.0 – 8.0. Darker the color was higher amount of magnetite was produced in the solution concerning the results from XRD analysis.

XRD analysis evidenced the proposed mechanism of magnetite formation revealing other system phase as Goethite ($Fe(OH)_2$) and magnetite phase existing together early in the precipitation process, as could be seen on pH 6.2 XRD result. The Goethite was consumed later in the process in transformation to the magnetite pH 10.1. When TIPP coating was applied to the prepared magnetite particles (pH 10.1), after sintering process the evidence of anatase formation on the magnetite surface is showed in both XRD and SEM analysis. Magnetite phase with anatase coating can be found despite of low quality of XRD results which could be partially caused by possible formation of amorphous $TiO_2$ phase over the magnetite.

SEM analysis was done to estimate if the surface morphology of prepared coated magnetic particles was changed. Magnetite particles were found to form round shaped clusters with average size distribution around 0.1 µm. After coating of particles with TIPP the higher size distribution was observed with particles covered by $TiO_2$, which was confirmed by SEM –EDS analysis.

## 5. CONCLUSION

Preparation of high purity particles of magnetite can be accomplished by slow precipitation of Mohric salt solution with sodium hydroxide solution in pH region above 10.0 in anaerobic conditions. Other phase presented during reaction was Goethite, which disappeared due to the consumption of hydroxyl groups for the formation of magnetite ($Fe_3O_4$). Simple process for coating of magnetite particles was verified resulting in formation of the anatase $TiO_2$ layer on their surface. Higher size distribution and change in the surface morphology of particles after TIPP coating is observed. There is possibility, that partially amorphous phase of $TiO_2$ is formed on the surface using sintering at 360°C in this process.

## ACKNOWLEDGEMENT

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